

# ISOTOPE SHIFTS IN $2^1P$ AND $2^3P$ STATES OF He AND $Li^{+}$

by

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Over the past few years there appeared several papers on the quantum mechanical three-body problem in which the exact dependence of the Hamiltonian on the masses has been taken into account.<sup>1-6</sup> The interest in this problem has been aroused by the need for a more direct approach in describing a system of three particles of nearly equal masses, since the usual approximation of infinitely heavy (stationary) nuclei obviously cannot be made. In such a case the non-relativistic and spin-free Hamiltonian of the system is expressed in terms of center-of-mass coordinates, and the Schrodinger equation becomes separable into two parts, the one describing the motion of the particles around the center of mass being the only one of interest here. With the exception of the paper by Kolos et al all the work done so far has been on the ground states (zero angular momentum) of molecular-like systems. The present note is a preliminary report on some calculations on atomic ions. We have set out to consider systems of three particles (two of which are identical) with total angular momentum equal to unity. While application to molecular and mesonic systems is desirable and is at present being carried out, we felt that calculations on atomic systems would not be without interest.

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In 1930 Hughes and Eckart<sup>7</sup> have employed center-of-mass coordinates to achieve the separation of the translational motion of the center of mass and the internal motion of a system of three particles. Assuming a simple open shell hydrogen-like wavefunction they have, by perturbation theory, obtained an analytical expression for the mass effect of a two-electron atom. When experimental methods became sufficiently refined to allow accurate measurements to be made on the isotope shift in helium it was found that the values of the isotope shift calculated from Hughes and Eckart's formula were in quantitative disagreement with the experimental results.<sup>8,9</sup> The discrepancy was especially pronounced in P states. Except for possibly a few unsuccessful attempts<sup>10</sup> there has been no further theoretical work done along these lines for excited states, mainly due to the lack of sufficiently accurate wavefunctions. Bethe and Salpeter have stated that "the cause of these discrepancies is not yet known,"<sup>11</sup> while others<sup>12</sup> have suspected the theory itself. The results reported here were obtained by applying the variational procedure to 50-term wavefunctions of the type 
$$\Psi = \sum c_{lmn} r_{12}^m r_{23}^l r_{31}^n D_{\mu',0}^1(\alpha, \beta, \gamma) \exp[1/2(-ar_{23} - br_{31})],$$
 where the  $r_{ij}$ 's are the interparticle distances,  $\alpha, \beta, \gamma$  are three Eulerian angles, and the  $D_{\mu',0}^1(\alpha, \beta, \gamma)$  are the appropriate elements of the three-dimensional rotational matrix corresponding to a space-z-component of the angular momentum  $M_z = 0$  and a body-z-component  $\mu'$ . The non-linear parameters

a and b were taken to be the same as those determined by minimizing the infinite mass energies. The linear constants  $c_{lmn}$  were determined in the usual manner from a secular equation and are, of course, different for each separate energy calculation.

If we define the mass ratio  $\rho = m/M$ , where m and M are the electronic and nuclear masses, respectively, then the computed energy, E, will depend on both the choice of units and the mass ratio  $\rho$ . Consequently, we write  $E = E(\rho)$ , and adopt the atomic units  $\mu e^4 h^{-2}$  for energy and  $h^2 \mu^{-1} e^{-2}$  for length. Note that the reduced mass,  $\mu$ , depends on  $\rho$ , i.e.  $\mu = m/(1+\rho)$ . The connection with experiment is made through the difference of the spectroscopic term values for two isotopes of the same atom<sup>13</sup>. The spectroscopic term value is the total (two-electron) atomic energy,  $E(\rho)$ , less the corresponding hydrogen-like (one-electron) energy,  $-1/2Z^2$ . The results are shown in Table I. The discrepancy between theory and experiment has now been brought within the limits of experimental accuracy. On the basis of the agreement for helium, we feel that it can be said with some confidence that the calculated results for  $Li^+$  are accurate to within one per cent.

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### Footnotes

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7. D. S. Hughes and C. Eckart, Phys. Rev. 36, 694 (1930).
8. L. C. Bradley and H. Kuhn, Proc. Royal Soc. A 209, 325 (1951).
9. M. Fred, F. S. Tomkins, J. K. Brody, and M. Hamermesh, Phys. Rev. 82, 406 (1951).
10. E.g. see ref. 9, footnote 30.
11. H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One and Two Electron Systems, Handbuch der Physik, Vol. XXXV, 1, p. 256 (Springer Verlag, Berlin, 1957).
12. See ref. 8.
13. The total mass effect has usually been thought of as consisting of two parts: an elementary mass correction in energy,  $\epsilon_1$ , due to the motion of the nucleus, and a much smaller correction,  $\epsilon_2$ , arising from the mass polarization (specific shift). Both of these corrections can be computed from our tabulated data, if required. The elementary correction,  $\epsilon_1$ , is given by  $\epsilon_1 = -p\epsilon(0)$ , while the second part,  $\epsilon_2$ , proportional to the expectation value of the operator  $\nabla_1 \cdot \nabla_2$ , is obtained by subtracting  $\epsilon_1$  from the total mass effect.

TABLE 1. Energy Values and Isotope Shifts

System	Rydberg( $\text{cm}^{-1}$ )	$\rho \times 10^4$	$E(\phi)(\text{a.u.})$	$E(\rho)(\text{a.u.})$	Calcd. Shift ( $\text{cm}^{-1}$ )	Experiment( $\text{cm}^{-1}$ )
$2^1\text{P}, \text{He}^3$	109717.345	1.81922	-2.12384187	-2.12383350	1.67	$1.68 \pm .005^b$
$2^1\text{P}, \text{He}^4$	109722.267	1.37058		-2.12383556	$(1.58)^a$	$1.67^c$
$2^1\text{P}, (\text{Li}^+)^6$	109727.295	0.91262	-4.99334925	-4.99332634	2.14	-----
$2^1\text{P}, (\text{Li}^+)^7$	109728.723	0.78211		-4.99332961	$(2.032)^a$	
$2^3\text{P}, \text{He}^3$	109717.345	1.81922	-2.13316322	-2.13317497	0.68	$0.675^c$
$2^3\text{P}, \text{He}^4$	109722.267	1.37058		-2.13317207	$(0.745)^a$	
$2^3\text{P}, (\text{Li}^+)^6$	109727.295	0.91262	-5.02771484	-5.02774269	0.66	-----
$2^3\text{P}, (\text{Li}^+)^7$	109728.723	0.78211		-5.02773871	$(0.653)^a$	

<sup>a</sup>Calculated from the Hughes-Eckart Formula, loc. cit.

<sup>b</sup>Bradley and Kuhn, loc. cit.

<sup>c</sup>Fred et al, loc. cit.